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(54) Title: IODOBENZOPYRAN-4-ONE DERIVATIVES HAVING FUNGICIDAL ACTIVITY

(57) Abstract: The present invention relates to iodobenzopyran-4-one derivativespossessing fungicidal properties against phytopathogenic organisms, amethod for preparing some of these derivatives, their use for protectingplants, and fungicidal compositions comprising such derivatives incombination with one or more other fungicidal compounds.

lodobenzopyran-4-one derivativeshaving fungicidal activity Description

The present invention relates to iodobenzopyran-4-one derivatives possessing fungicidal properties against phytopathogenic organisms, a method for preparing some of these derivatives, their use for protecting plants, and fungicidal compositions comprising such derivatives in combination with one or more other fungicidal compounds.

International Patent Application WO-97/13762 describes in particular derivatives of the halobenzopyranone type. This document discloses a very large number of compounds by means of a very general chemical formula. However, the compounds given as examples are essentially compounds carrying a bromine atom or a carbon chain on the benzene ring. Thus, this document focuses on compounds which are not substituted with an iodine atom as is the case of the present invention. Indeed, only two iodinated compounds are disclosed by this document without however indicating that such compounds can possess properties which are superior to the other derivatives, in particular the brominated derivatives.

It has now been discovered that certain particular iodobenzopyran-4-one derivatives possess excellent fungicidal properties against phytopathogenic organisms. These properties may be further improved when these compounds are used as a mixture with one or more other fungicidal compounds.

A first aspect of the present invention relates to the compounds of formula (I)

$$\begin{array}{c|c}
0 & R^1 \\
\hline
 & Q & R^2
\end{array}$$
(I)

in which:

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- the iodine atom is placed in the 5, 6, 7 or 8 position;
- R^1 is chosen from a halogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical;

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- R^2 is chosen from a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, a halogen atom, the cyano radical, the radical -W- R^3 ;
 - W is chosen from oxygen, sulphur or the radical -NR⁴;
- R^3 and R^4 , which are identical or different, are chosen, independently of each other, from the hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, an alkoxy radical, an amino radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, R^3 and R^4 may form together a 5- to 7-membered heterocycle which may be saturated, unsaturated or aromatic, and which may also comprise another heteroatom; and their possible geometric and/or optical isomers, in pure form or in the form of mixtures, in any proportions, including the racemic mixture(s), their possible N-oxides, addition salts with an acid, and their possible metal or metalloid complexes; R^3 being different from the methyl radical or the butyl radical when the iodine is in the 6-position, when R^1 is the n-propyl radical and when W represents oxygen.

When the radicals of the compounds of formula (I) are substituted, they are substituted in a preferred manner with one or more groups which may be chosen independently of each other from alkyl, alkenyl and alkynyl radicals, a halogen atom, the cyano, trialkylsilyl, alkoxy, alkylthio, hydroxyl, nitro, amino, acyl, acyloxy, phenyl, heterocyclyl, phenylthio, phenoxy, heterocyclyloxy or

heterocyclylthio radical and oxidized derivatives and may be optionally substituted with chemical entities containing a thio group.

The term heterocyclyl comprises heteroaryl groups and non-aromatic heterocyclyl groups which may be saturated or unsaturated.

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The heteroaryl groups are generally 5- or 6-membered rings containing up to 4 heteroatoms chosen from nitrogen, oxygen and sulphur, optionally fused with a benzene ring. As examples of heteroaryl groups, there especially may be mentioned groups derived from thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, indazole, benzothiadiazole, benzotriazole, dibenzofuran. dibenzothiophene, carbazole, pyridine, pyrazine, pyrimidine, pyridazine, 1,3,5triazine, 1,2,4-triazine, 1,2,4,5-tetrazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine, 1,6-naphthyridine, 1,7-naphthyrdine, phthalazine, pyridopyrimidine, purine or pteridine.

The non-aromatic heterocyclyl groups are generally 3-, 5-, 6- or 7-membered rings containing up to 3 heteroatoms chosen from nitrogen, oxygen and sulphur, for example oxiranyl, thiiranyl, thiazolinyl, dioxolanyl, 1,3-benzothiazinyl, morpholino, pyrazolinyl, sulpholanyl, dihydroquinazolinyl, piperidinyl, phthalimido, tetrahydrofuranyl, tetrahydropyranyl, pyrrolidinyl, indolinyl, 2-oxopyrrolidino, 2-oxobenzoxazolin-3-yl or tetrahydroazepinyl.

The substituents, when they are present, on the phenyl or heterocyclyl groups may, for example, be halogen atoms, CN, NO_2 , SF_5 , $B(OH)_2$, trialkylsilyl, acyl, O-acyl or a radical E, OE or $S(O)_n$ E as defined above for R^2 or alternatively is an optionally substituted amino radical; or alternatively two adjacent groups on the ring, together with the atoms to which they are attached,

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form a carbocyclic or heterocyclic ring which may be optionally substituted in a similar manner.

The term acyl comprises the acid residues containing sulphur or phosphorus and the carboxylic acid residues. Examples of acyl groups are thus $-\text{COR}^5$, $-\text{COOR}^5$, $-\text{CINR}^5\text{R}^6$, $-\text{CON}(\text{R}^5)\text{OR}^6$, $-\text{COONR}^5\text{R}^6$, $-\text{CON}(\text{R}^5)\text{NR}^6\text{R}^7$, $-\text{COSR}^5$, $-\text{CSSR}^5$, $-\text{S}(\text{O})_q\text{R}^5$, $-\text{S}(\text{O})_2\text{OR}^5$, $-\text{S}(\text{O})_q\text{NR}^5\text{R}^6$, $-\text{P}(=\text{L})(\text{OR}^5)(\text{OR}^6)$ or $-\text{COOR}^5$, in which R^5 , R^6 and R^7 , which may be identical or different, represent the hydrogen atom, an optionally substituted alkyl radical, an optionally substituted cycloalkenyl radical, an optionally substituted alkenyl radical, an optionally substituted alkenyl radical, an optionally substituted alkynyl radical, an optionally substituted phenyl group or an optionally substituted heterocyclyl group, or alternatively R^5 and R^6 , or R^6 and R^7 , together with the atom(s) to which they are attached, may form a ring, q represents 1 or 2 and L represents O or S.

The amino radicals may be substituted, for example, with one or two optionally substituted alkyl or optionally substituted acyl radicals, or alternatively two substituents may form a ring, preferably a 5- to 7-membered ring, which may be substituted and which may contain other heteroatoms, and for example morpholine.

Among the compounds of formula (I) there are preferred those possessing at least one of the following characteristics:

- the iodine atom is in the 6-position;
- R¹ represents a C₂-C₄ alkyl radical;
- R² represents the radical -W-R³ in which W represents oxygen and R³ is as defined above.

The most preferred compounds of formula (I) simultaneously possess these three characteristics, in particular the compounds of formula (I) in which R^3 represents a C_1 - C_6 alkyl radical, a C_1 - C_6 alkenyl radical or a C_1 - C_6 alkynyl

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radical or alternatively the compounds of formula (I) in which R¹ is a n-propyl radical.

Among the compounds of formula (I), there may be mentioned, by way of examples, the following compounds of formulae (Ia) and (Ib) which do not limit the scope of the present invention:

$$\begin{array}{c|c}
 & O \\
 & O \\$$

Example	R1	R2
1	*	*
2	*	*
3	*	*
4	<i>X</i> ~	*~~
5	<i>x</i> ~~	*
6	*	*
7	*	*
8	*	*
9	*	*

$$\begin{array}{c|c}
O \\
\hline
O \\
\hline
O \\
7
\end{array}$$

$$\begin{array}{c|c}
\bullet \\
O \\
\hline
O \\
\hline
O \\
\end{array}$$

$$\begin{array}{c|c}
\bullet \\
O \\
\hline
O \\
\end{array}$$

$$\begin{array}{c|c}
\bullet \\
\hline
O \\
\end{array}$$

$$\begin{array}{c|c}
\bullet \\
\end{array}$$

$$\begin{array}{c|c}
\bullet \\
O \\
\end{array}$$

$$\begin{array}{c|c}
\bullet \\
\end{array}$$

$$\begin{array}{c|$$

Example		w	R1	R3
10	8-1	0	*	x
11	6-1	0	*	*
12	6-I	0	*~	₹ F F
13	6-I	0	<i>></i>	<i>x</i> ~
14	6-I	0	*	<i>x</i> ~°
15	6-I	0	*	*
16	6-I	0	<i>></i>	*
17	6-I	0	<i>></i> ~	*\
18	6-1	0	<i>>></i>	₹ F
19	6-l	0	*	***

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Example	l	w	R1	R3
20	6-I	0	*	***
21	6-I	0	¥	+
22	6-I	0	X	7
23	6-l	0	X	*
24	6-1	0	X	+
25	6-1	0	*X	<i>x</i> ~~
26	6-I	0	X	*
27	6-1	0	X	Х
28	6-I	0	X	×
29	6-1	0	x	Х

Example	1	w	R1	R3
30	6-1	0	*	F
31	6-1	0	*	+
32	6-1	0	*	<u></u>
33	6-1	0	<i>x</i> ~	*
34	6-1	0	+	*
35	6-1	0	*	**
36	6-1	0	*	F
37	6-I	0	*~	+
38	6-I	0	*~	+ _ s
39	6-I	0	*	, N

Example	1	w	R1	R3
40	6-1	0	*	*
41	6-1	0	÷	*
42	6-1	0	+	Q,
43	6-1	0	+	× °
44	6-1	0	÷/_	×.
45	6-1	0	4	
46	6-1	0	- -	. *_\
47	6-1	0	÷/	*_=
48	6-I	0	÷/	- }
49	6-1	0	4	*

			 	
Example	ı	W	/ R1	R3
50	6-1	0	*/	*
51	6-1	0	4	*
52	6-1	0	4	F
53	6-1	0	+	
54	6-1	0	*_	
55	6-1	0	÷/	→
56	6-I	0	4	→
57	6-1	0	*	+\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
58	6-I	0	₹	X
59	6-I	0	÷/	*

Example	1	w	R1	R3
60	6-I	0	*	X
61	6-1	0	*	*
62	6-l	0	*	*
63	6-1	0	*	*
64	6-I	0	*	*~
65	6-I	0	*	*
66	6-1	0	*	F
67	6-1	0	*	FF
68	6-1	0	*	1
69	6-1	0	*	1

Example	ı	w	R1	R3
70	6-I	0	*\	7
71	6-1	0	*	*_s_\
72	6-I	0	*	} H
73	6-I	0	4	*
74	1-6	0	4	→ a F
75	6-1	0	4	→ F
76	6-I	0	_X) A
77	6-l	0	*	*
78	6-I	0	4	**************************************
79	6-l	0	*	Br

Example	1	w	R1	R3
80	6-1	0	*	*
81	6-I	0	+	*
82	6-l	0	*	*
83	6-I	0	4	
84	6-I	0	+	
85	6-l	0	4	*
86	6-I	0	4	*
87	6-I	0	4	*
88	6-1	0	*	*

1	Example	l	w	R1	R3
	89	6-I	0	×~	*
	90	6-1	0	*~	*
	91	6-1	0	*	λ∕ F F
	92	6-l	0	*	*
	93	6-I	0	*	→
	94	6-1	0	*	***************************************
	95	6-1	0	*	H
	96	6-1	0	*	X
	97	6-I	0	*	***************************************
	98	6-1	NR4	*	R3=R4=H

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The compounds of the present invention may be prepared by numerous methods which are known procedures, in particular those disclosed in Patent Application EP-861 242.

In a particularly advantageous manner, the compounds of formula (I) may also be prepared according to the following method:

This method constitutes another aspect of this invention.

Other methods may also be used to prepare the compounds of formula (I), such as methods similar to those described in *Chemistry and Industry*, (1980), 116; *J. Chem. Soc. Chem. Com.*, <u>1</u>, (1981), 282 and *J. Org. Chem.*, (1992), <u>57</u>, 6502.

The reagents and some of the intermediate compounds useful for the preparation of the compounds of formula (I) may be prepared by methods known to persons skilled in the art.

Another aspect of the present invention relates to a fungicidal composition comprising

a) a compound of formula (I):

$$\begin{array}{c|c}
0 & R^1 \\
\hline
 & Q^2 & R^2
\end{array}$$
(I)

in which:

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- the iodine atom is placed in the 5, 6, 7 or 8 position;
- R^1 is chosen from a halogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical;
- R^2 is chosen from a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, a halogen atom, the cyano radical, the radical -W- R^3 ;
 - W is chosen from oxygen, sulphur or the radical -NR⁴;
- R^3 and R^4 , which are identical or different, are chosen, independently of each other, from the hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, an alkoxy radical, an amino radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, R^3 and R^4 may form together a 5- to 7-membered heterocycle which may be saturated, unsaturated or aromatic, and which may also comprise another heteroatom; and their possible geometric and/or optical isomers, in pure form or in the form of mixtures, in any proportions, including the racemic mixture(s), their possible N-oxides, addition salts with an acid, and their possible metal or metalloid complexes;
 - b) at least one other fungicidal compound.

The preferred compounds of formula (I) for the composition according to the invention are those possessing at least one of the following characteristics:

- the iodine atom is in the 6-position:
- R¹ represents a C₂-C₄ alkyl radical;

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- R² represents the radical -W-R³ in which W represents oxygen and R³ is as defined above.

The most preferred compounds of formula (I) for the composition according to the invention simultaneously possess these three characteristics, in particular the compounds of formula (I) in which R^3 represents a C_1 - C_6 alkyl radical, a C_1 - C_6 alkenyl radical or a C_1 - C_6 alkynyl radical or alternatively the compounds of formula (I) in which R^1 is a n-propyl radical.

There may be mentioned in particular the compounds whose chemical name is the following:

- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one,
- 2-ethoxy-6-iodo-3-propyl-benzopyran-4-one,
- 6-iodo-2-propoxy-3-propyl-benzopyran-4-one,
- 2-but-2-ynyloxy-6-iodo-3-propyl-benzopyran-4-one,
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one,
- 2-but-3-enyloxy-6-iodo-3-propyl-benzopyran-4-one,
- 3-butyl-6-iodo-2-isopropoxy-benzopyran-4-one,
- 6-iodo-3-propyl-2-(tetrahydro-pyran-4-yloxy)-benzopyran-4-one,
- 6-iodo-3-propyl-2-(2,2,2-trifluro-ethoxy)-benzopyran-4-one.

In the composition according to the invention, there is preferred the use of fungicidal compounds chosen from

b1) compounds capable of inhibiting the transport of electrons in the mitochondrial ubiquinol:ferricytochrome-c oxidoreductase respiratory chain of phytopathogenic fungal organisms, in particular strobilurin derivatives such as dimoxystrobin, fluoxastrobin, kresoxim-methyl, pycoxystrobin, pyraclostrobin, or fenamidone or famoxadone; or

b2) the compounds capable of inhibiting the biosynthesis of ergosterol, in particular compounds of the triazole type such as bromuconazole, epoxyconazole, fluquinconazole, prochloraz, prothioconazole, tebuconazole, triadimenol, triticonazole.

As other preferred compounds which may be used in the composition according to the invention, there may be mentioned cyprodinil, dinocap, fenpropidin, fenpropimorph, fosetyl, iprovalicarb, quinoxyfen, spiroxamine.

As particular combinations of compounds of formula (I) with one or more other fungicidal compounds, the following combinations are preferred:

Compounds of formula (I): Compound(s) b:

- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one +
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + pyraclostrobin
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + picoxystrobin
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + kresoxym-methyl
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluquinconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + tebuconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + prochloraz
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + prothioconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + triadimefon
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + triadimenol
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + triticonazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + epoxiconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + dinocap
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + spiroxamine
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fenpropidin
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fenpropimorph
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + quinoxyfen
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + cyprodinil
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fosetyl-Al
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fenamidone
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + iprovalicarb
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluoxastrobin
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one +
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + pyraclostrobin
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + picoxystrobin
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + kresoxym-methyl
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluquinconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + tebuconazole

- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + prochloraz
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + prothioconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + triadimefon
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + triadimenol
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + triticonazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + epoxiconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + dinocap
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + spiroxamine
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fenpropidine
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fenpropimorphe
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + quinoxyfen
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + cyprodinil
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fosetyl-al
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fenamidone
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + iprovalicarb
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluoxastrobin
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one +
 - + fluquinconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one +
 - + tebuconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one +
 - + prochloraz
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one +
 - + prothioconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one +
 - + spiroxamine
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluoxastrobin
 - + fluquinconazole

- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluoxastrobin + tebuconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluoxastrobin+ prochloraz
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluoxastrobin
 + prothioconazole
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fluoxastrobin
 + spiroxamine
- 2-butoxy-6-iodo-3-propyl-benzopyran-4-one + fosetyl-al + fenamidone
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + trifloxystrobine
 + fluquinconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one +
 + prochloraz
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one +
 + prothioconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one +
 + spiroxamine
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluoxastrobin
 + fluquinconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluoxastrobin
 + tebuconazole
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluoxastrobin
 + prochloraz
- 6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluoxastrobin
 + prothioconazole

WO 03/014103

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6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fluoxastrobin

21

+ spiroxamine

PCT/EP02/09418

6-iodo-2-(1-methyl-butoxy)-3-propyl-benzopyran-4-one + fosetyl-Al

+ fenamidone

It has been possible to demonstrate a synergistic effect linked to the use of the composition according to the invention.

For their use, the compounds of formula (I) and the compositions comprising a compound of formula (I) combined with one or more other fungicidal compounds are usually mixed with a carrier and a surfactant which are acceptable for use in agriculture.

The carrier or diluent in the composition according to the present invention may be a solid or a liquid, optionally in combination with a surfactant, for example a dispersing agent, an emulsifying agent or a wetting agent.

Suitable surfactants comprise anionic compounds such as a carboxylate, for example a metal carboxylate having a long chain fatty acid; a Nacylsarcosinate; mono- or diesters of phosphoric acid with fatty alcohol ethoxylates or alternatively salts of the said esters; fatty alcohol sulphates such as sodium dodecyl sulphate, sodium octadecyl sulphate or sodium cetyl sulphate; ethoxylated fatty alcohol sulphates; ethoxylated alkylphenol sulphates; lignosulphonates; petroleum sulphonates; alkylaryl sulphonates such as alkylbenzene sulphonates or low alkylnaphthalene sulphonates, for example butylnaphthalene sulphonates; salts of sulphonated naphthalene-formaldehyde condensates; salts of sulphonated phenol-formaldehyde condensates; or even more complex sulphonates such as amidesulphonates, for example the sulphonated product of condensation of oleic acid with N-methyltaurine or dialkyl sulphosuccinates, for example sodium sulphonate of dioctyl succinate. Among the nonionic agents, there may be mentioned the products of condensation of esters of fatty acids, of fatty alcohols, of amides of fatty acids or of phenols substituted by fatty alkyls or alkenyls with ethylene oxide, fatty esters of ethers of polyhydric alcohols, for example sorbitan fatty acid esters, products of condensation of the said esters with ethylene oxide, for example fatty acid esters of polyoxyethylene sorbitan, block copolymers of ethylene and

22

propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, or ethoxylated acetylenic glycols.

Among the cationic surfactants, there may be mentioned, for example, an aliphatic mono-, di- or polyamine in acetate, naphthenate or oleate form; an oxygen-containing amine such as an amine oxide or a polyoxyethylene alkylamine; an amine containing an amide bond prepared by condensation of a carboxylic acid with a diamine or a polyamine; or a quaternary ammonium salt.

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The compositions according to the present invention may take any forms known in the art of formulating agrochemical compounds, for example, a solution, dispersion, aqueous emulsion, pulverulent powder,

formulation for fumigation or smoking, dispersible powder, emulsifiable concentrate or granules. Furthermore, they may be in a form suitable for direct use or in a concentrated form or in the form of a primary composition requiring dilution with a suitable quantity of water or another diluent before application.

The concentration of active ingredient(s) in the composition of the present invention, as applied to plants, is preferably in the range between 0.0001 to 1.0% by weight, particularly 0.0001 and 0.01% by weight. In a primary composition, the quantity of active ingredient may vary considerably and may be, for example, between 5 and 95% by weight of composition.

The compounds of formula (I) of the present invention,

possess activity as a fungicide, particularly against fungicidal diseases of plants, for example powdery mildews and downy mildews and particularly cereal powdery mildew (*Blumeria graminis*), vine powdery mildew (*Uncinula necator*), apple powdery mildew (*Podosphaera leucotricha*), cucurbit powdery mildews (for example *Erysiphe cichoracearum, Sphaerotheca fuliginea, Erysiphe polygoni*), powdery mildew of Solanaceae (for example *Leveillula taurica*), powdery mildew of fruit and ornamental plants (for example *Sphaerotheca pannosa*), vine downy mildew (*Plasmopara viticola*), rice blight cereal eyespot (*Pseudocercosporella herpotrichoides*), rice sheath blight (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), damping off (*Rhizoctonia solani*), wheat brown rust (*Puccinia recondita*), tomato or potato

23

blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*), glume blotch (*Leptosphaeria nodorum*).

The compounds of formula (I) may also prove to be active on other phytopathogenic fungi, including other types of powdery mildew, rusts, as well as general pathogens originating from Deuteromycetes, Ascomycetes, Phycomycetes and Basidiomycetes.

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The compounds of formula (I) according to the present invention have proved particularly active against powdery mildews of cereals, vine, plants and fruit trees, vegetable crops and ornamental plants.

Another aspect of the invention therefore also relates to a method for controlling phytopathogenic fungi of crops at a site which is infested or which may be infested by them, which comprises the application to the said site of at least one compound of formula (I), alone or in combination with one or more other fungicidal compounds as described above, notably within a composition according to the present invention.

An alternative consists in applying the active ingredient directly to the plant, for example by spraying or dusting, either when the phytopathogenic fungus has started to appear on the plant, or before the appearance of the said fungus as a preventive measure, or preventively and curatively. In each of these cases, the preferred method of application is foliar spraying. It is generally important to obtain good control of phytopathogenic fungi during the

first stages of plant growth, these stages being the precise moments when the plants may be the most seriously damaged. It is sometimes advantageous to treat the roots of the plant before or during planting, for example by dipping the roots in a composition comprising a compound of formula (I).

The invention is illustrated without limitation by the following examples.

Example of test N°1

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The compounds were tested for their activity against wheat powdery mildew (*Blumeria graminis*).

Winter wheat (Appolo variety) was planted in France (department of Marne) in 1 m² plots, at the rate of 200 kg/ha (soil: coloured rendzina) at a depth of 3 cm.

The compounds of the invention were applied to the wheat plants in two portions: Application A at the 1 cm ear stage and then Application B at the second visible node stage. Each of these applications was carried out by spraying an aqueous solution of the compounds at a dose of 125 g of active ingredient/ha.

During Application A, the intensity of attack by the fungus *Blumeria graminis* is estimated at 3% of the total foliar volume.

The tests of intensity of attack are carried out 52 days after Application B by evaluating the percentage of affected surface area of the second leaves (counted from the ear).

The results presented in Table 1 were obtained with the following compounds according to the invention:

Compound 1: 2-ethoxy-6-iodo-3-propylbenzopyran-4-one

Compound 2: 6-iodo-2-propoxy-3-propylbenzopyran-4-one

Compound 3: 2-butoxy-6-iodo-3-propylbenzopyran-4-one

Control: untreated plants and Compound B: quinoxyfen (commercial reference Fortress®).

Compound	% affected surface area per (second) leaf
1	0.56
2	2.53
3	2.51

Control	30.47
Α	6.47
В	4.91

Table 1 (Test of intensity of attack)

Under the same conditions, a test of frequency of attack was performed by evaluating the percentage of second leaf (from the ear) attacked by the fungus *Blumeria graminis*.

5 The results obtained are presented in Table 2.

Compound	% of second leaf attacked
1	28.0
3	54.0
Control	98.7
A	78.7
В	73.3

Table 2 (Test of frequency of attack)

The results of these two tests show that the iodinated compounds of formula (I) according to the present invention are active compared with the untreated control, and also more active than the commercial reference.

Example of test N°2

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This example gives an illustration of the biological efficacy of the compounds of formula (I) on pathogenic strains resistant to strobilurin derivatives.

The experiment was performed in a greenhouse.

- Resistant strains were isolated and samples taken in 2001 in the north of Germany in the Bremen region in a place treated with pyraclostrobin and with picoxystrobin. These strains are characterized by their resistance to these strobilurin-type compounds. They were then kept in a controlled-environment chamber on wheat plants (Kanzler variety) treated with
- The tested compounds were sprayed on the wheat plants using solutions for application diluted in water to a volume equivalent to 250 l/ha. 24 h later, the plants were inoculated with powdery mildew (*Blumeria graminis f. sp. tritici*).

The extent of the disease was evaluated on each plant after 13 days of incubation.

The results obtained are assembled in Table 3 and show that the compound used allows complete control of the strains treated. These results can be applied to conditions of use in the open field.

Compound applied	quantity	Percentage of leaves
	applied	affected by powdery
	(g/ha)	mildew
		(%)
Control plants without treatment	-	100
	31	100
(EC at 125 g/l - Twist [®]	62	100
	125	100
	250	100
2-ethoxy-6-iodo-3-	31	0
propylbenzopyran-4-one	62	0
(SC at 500 g/l)		

Table 3

Example of test N°3

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This example gives an illustration of the synergistic effect obtained using the compounds according to the invention in the form of a mixture with compounds of the strobilurin type, in particular triazole, in particular fluquinconazole. The compounds according to the invention were tested in a greenhouse under preventive conditions. This synergistic effect was demonstrated on the principal diseases affecting cereals, in particular wheat and barley powdery mildews (*Blumeria graminis f. sp. tritici* and *Blumeria graminis f. sp. hordei*), wheat brown rust (*Puccinia recondita*) and wheat glume blotch (*Septoria tritici* and *Septoria nodorum*).

The combinations of active ingredients in Table 4 were evaluated.

Active ingredient(s)	Ratio	Applied doses (g/ha)	
_ , .		, , ,	

2-ethoxy-6-iodo-3-propylbenzopyran-4-one	-	1.5, 3, 4, 6, 8, 12, 16,
(SC at 500 g/l)		25, 31, 50, 62
fluquinconazole	-	3, 6, 8, 12, 16, 25, 31,
(SC at 100 g/l - Flamenco [®])		50, 62, 125
	_	4, 8, 16, 31, 62, 125
(WG at 500 g/kg - Flint [®])		
2-ethoxy-6-iodo-3-propylbenzopyran-4-one	1/1	
(SC at 500 g/l)	1/2.5	
+	1/5	
(WG at 500 g/kg)		,
2-ethoxy-6-iodo-3-propylbenzopyran-4-one	1/1	
(SC at 500 g/l)	1/2	
+	1/5	
fluquinconazole		
(SC at 100 g/l)		

Table 4

The epoxyconazole and kresoxim-methyl mixture (SC 125 g/l + 125 g/l - Ogam[®]) was used as reference at the recommended doses for application of 62+62 g/ha and 125+125 g/ha.

5 The compounds and mixtures tested were sprayed on wheat plants:

- two replications,

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- volume for application equivalent to 250 l/ha.

On the day following the application, the wheat plants were inoculated with powdery mildew (*Blumeria graminis f. sp. tritici*), brown rust (*Puccinia recondita*), glume blotches (*Septoria tritici* and *Septoria nodorum*) and the barley plants with powdery mildew (*Blumeria graminis f. sp. hordei*).

Once the diseases had developed, the evaluation was made by determining the extent of disease per pot.

The level of synergy was calculated using the Colby formula in order to calculate the theoretical efficacy and to compare it to the observed efficacy:

Theoretical efficacy of A + B = efficacy of A (%) + efficacy of B (%)

WO 03/014103

- [efficacy of A (%) × efficacy of B (%)/100]

If the observed efficacy is higher than the theoretical efficacy, a synergistic effect is demonstrated; if it is equal, an additive effect is demonstrated; if it is lower, an antagonist effect is demonstrated.

The results obtained for a mixture of compound of formula (I) according to the invention and fluquinconazole for controlling wheat powdery mildew are assembled in Table 5.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
,	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	6	-	25		-
propylbenzopyran-4-one					
fluquinconazole	6	-	0	-	-
	12	-	0	-	
	31	-	0	-	-
2-ethoxy-6-iodo-3-	6+6	1/1	93	25	+68
propylbenzopyran-4-one	6+12	1/2	90	25	+65
+ fluquinconazole	6+31	1/5	95	25	+70

Table 5

The results obtained for a mixture of compound of formula (I) according to the invention and fluquinconazole for controlling barley powdery mildew are assembled in Table 6.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	12	-	50	-	-
propylbenzopyran-4-one					
fluquinconazole	12	-	25	-	-
	25	-	25	-	-

	62	-	75	-	
2-ethoxy-6-iodo-3-	12+12	1/1	90	62.5	+28
propylbenzopyran-4-one	12+25	1/2	95	62.5	+33
+ fluquinconazole	12+62	1/5	98	87.5	+11

Table 6

The results obtained for a mixture of compound of formula (I) according to the invention and fluquinconazole for controlling wheat brown rust are assembled in Table 7.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	50	-	0	-	-
propylbenzopyran-4-one				:	
fluquinconazole	100	-	60	-	_
2-ethoxy-6-iodo-3-	50 + 100	1/2	90	60	+30
propylbenzopyran-4-one+					
fluquinconazole					

Table 7

The results obtained for a mixture of compound of formula (I) according to the invention and fluquinconazole for controlling wheat glume blotch (*Septoria tritici*) are assembled in Table 8.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	50	-	0	-	-
propylbenzopyran-4-one					
fluquinconazole	100	-	60	-	-
2-ethoxy-6-iodo-3-	50 + 100	1/2	90	60	+30
propylbenzopyran-4-one+					
fluquinconazole					

Table 8

The results obtained for a mixture of compound of formula (I) according to the invention and fluquinconazole for controlling wheat glume blotch (*Septoria nodorum*) are assembled in Table 9.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	50	-	0	•	-
propylbenzopyran-4-					
one					
fluquinconazole	100	-	. 75	h	1
2-ethoxy-6-iodo-3-	50 + 100	1/2	95	75	+20
propylbenzopyran-4-one					
+ fluquinconazole					

Table 9

These results demonstrate a high synergistic effect of the mixtures of compound of formula (I) and fluquinconazole in ratios of 1/1, 1/2 or 1/5 against wheat and barley powdery mildews, wheat brown rust and glume blotches. These mixtures make it possible to obtain excellent results of efficacy at agronomic doses for application.

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The results obtained for a mixture of compound of formula (I) according to the invention and for controlling wheat powdery mildew are assembled in Table 10.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
:	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	6	-	25		
propylbenzopyran-4-one	16	-	50	-	-
	25	-	75		
	16	-	30	-	-
	31	-	40		

	62	-	50		
2-ethoxy-6-iodo-3-	16+16	1/1	95	65	+30
propylbenzopyran-4-one	25+62	1/2.5	95	87.5	+8
+	6+31	1/5	85	55	+30

Table 10

The results obtained for a mixture of compound of formula (I) according to the invention and for controlling barley powdery mildew are assembled in Table 11.

Active ingredient(s)	Dose for	Ratio	Observed	Theoretical	Level of
	application		efficacy	efficacy	synergy
	(g/ha)		(%)	(%)	
2-ethoxy-6-iodo-3-	16	-	50	_	-
propylbenzopyran-4-one	25	-	75		<u> </u>
	16	-	0	-	-
	62	-	0		
2-ethoxy-6-iodo-3-	16+16	1/1	75	50	+25
propylbenzopyran-4-one+	25+62	1/2.5	85	75	+10

Table 11

These results demonstrate a high synergistic effect of the mixtures of compound of formula (I) and in ratios of 1/1, 1/2.5 or 1/5 against wheat and barley powdery mildews (on strains sensitive to compounds of the strobilurin type).

Claims

1. Compound of formula (I):

$$\begin{array}{c|c}
O & & \\
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O & &$$

in which:

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- the iodine atom is placed in the 5, 6, 7 or 8 position;
- R^1 is chosen from a halogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical;
- R^2 is chosen from a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, a halogen atom, the cyano radical, the radical -W- R^3 ;
 - W is chosen from oxygen, sulphur or the radical -NR⁴;
- R^3 and R^4 , which are identical or different, are chosen, independently of each other, from the hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, an alkoxy radical, an amino radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, R^3 and R^4 may form together a 5- to 7-membered heterocycle which may be saturated, unsaturated or aromatic, and which may also comprise another heteroatom;

and their possible geometric and/or optical isomers, in pure form or in the form of mixtures, in any proportions, including the racemic mixture(s), their possible N-oxides, addition salts with an acid, and their possible metal or metalloid complexes; R³ being different from the methyl radical or the butyl

WO 03/014103

radical when the iodine is in the 6-position, when R¹ is the n-propyl radical and when W represents oxygen.

- 2. Compound according to Claim 1, for which the iodine atom is in the 6-position.
- 3. Compound according to either of Claims 1 and 2, for which R² is a radical -W-R³.
 - 4. Compound according to Claim 3, for which W represents oxygen.
- 5. Compound according to any one of Claims 1 to 4, for which R^3 is a C_1 - C_6 alkyl radical, a C_1 - C_6 alkenyl radical or a C_1 - C_6 alkynyl radical.
- 6. Compound according to any one of Claims 1 to 5, for which R^1 is a C_1 - C_6 alkyl radical.
- 7. Compound according to Claim 6, for which R¹ is a n-propyl radical.
 - 8. Method for preparing a compound of formula (I)

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$$\begin{array}{c|c}
 & O \\
 & O \\$$

in which:

- the iodine atom is placed in the 5, 6, 7 or 8 position:
- R^1 is chosen from a halogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical;
- R^2 is chosen from a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, a halogen atom, the cyano radical, the radical -W- R^3 ;
 - W is chosen from oxygen, sulphur or the radical -NR⁴;

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- R^3 and R^4 , which are identical or different, are chosen, independently of each other, from the hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, an alkoxy radical, an amino radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, R^3 and R^4 may form together a 5- to 7-membered heterocycle which may be saturated, unsaturated or aromatic, and which may also comprise another heteroatom;

and their possible geometric and/or optical isomers, in pure form or in the form of mixtures, in any proportions, including the racemic mixture(s), their possible N-oxides, addition salts with an acid, and their possible metal or metalloid complexes; comprising the following steps:

- 9. Fungicidal composition comprising
- a) a compound of formula (I):

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in which:

- the iodine atom is placed in the 5, 6, 7 or 8 position;
- R^1 is chosen from a halogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical;
- R^2 is chosen from a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, a halogen atom, the cyano radical, the radical -W- R^3 ;
 - W is chosen from oxygen, sulphur or the radical -NR⁴;
- R^3 and R^4 , which are identical or different, are chosen, independently of each other, from the hydrogen atom, a substituted or unsubstituted C_1 - C_6 alkyl radical, a substituted or unsubstituted C_1 - C_6 alkenyl radical and a substituted or unsubstituted C_1 - C_6 alkynyl radical, an alkoxy radical, an amino radical, a 3- to 7-membered carbo- or heterocycle which is substituted or unsubstituted and which may be saturated, unsaturated or aromatic, R^3 and R^4 may form together a 5- to 7-membered heterocycle which may be saturated, unsaturated or aromatic, and which may also comprise another heteroatom;

and their possible geometric and/or optical isomers, in pure form or in the form of mixtures, in any proportions, including the racemic mixture(s), their possible N-oxides, addition salts with an acid, and their possible metal or metalloid complexes;

- b) at least one other fungicidal compound.
- 10. Composition according to Claim 9, comprising a compound of formula (I) in which the iodine atom is in the 6-position.
- 11. Composition according to either of Claims 9 and 10, comprising a compound of formula (I) in which R² is a radical -W-R³.
- 12. Composition according to Claim 11, comprising a compound of formula (I) in which W represents oxygen.

WO 03/014103 PCT/EP02/09418

- 13. Composition according to either of Claims 11 and 12, comprising a compound of formula (I) in which R^3 is a radical chosen from a C_1 - C_6 alkyl radical, a C_1 - C_6 alkenyl radical or a C_1 - C_6 alkynyl radical.
- 14. Composition according to any one of Claims 9 to 13, comprising a compound of formula (I) in which R^1 is a C_1 - C_6 alkyl radical.

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- 15. Composition according to Claim 14, comprising a compound of formula (I) in which R¹ is a n-propyl radical.
- 16. Composition according to any one of Claims 9 to 15, comprising, as compound b) a fungicidal compound chosen from
- b1) compounds capable of inhibiting the transport of electrons in the mitochondrial ubiquinol:ferricytochrome-c oxidoreductase respiratory chain of phytopathogenic fungal organisms, or
 - b2) the compounds capable of inhibiting the biosynthesis of ergosterol.
- 17. Composition according to Claim 16, comprising as compound b1) a fungicidal compound chosen from strobilurin derivatives, fenamidone or famoxadone.
- 18. Composition according to Claim 17, comprising a strobilurin derivative chosen from azoxystrobin, dimoxystrobin, fluoxastrobin, kresoximmethyl, pycoxystrobin, pyraclostrobin,
- 19. Composition according to Claim 16, comprising as compound b2) a triazole-type fungicidal compound.
- 20. Composition according to Claim 19, comprising a triazole-type compound chosen from bromuconazole, epoxyconazole, fluquinconazole, prochloraz, prothioconazole, tebuconazole, triadimefon, triadimenol, triticonazole.
- 21. Composition according to Claim 16, comprising as compound b) a compound chosen from cyprodinil, dinocap, fenpropidin, fenpropimorph, fosetyl, iprovalicarb, quinoxyfen, spiroxamine.
- 22. Method for controlling phytopathogenic fungi of crops at a site which is infested or which may be infested by them, which comprises the application to the said site of at least one compound of formula (I) according to any one of Claims 1 to 7 Claims.

37

23. Method for controlling phytopathogenic fungi of crops at a site which is infested or which may be infested by them, which comprises the application to the said site of at least one composition according to any one of Claims 9 to 21.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D311/56 C07D311/22 A01N43/16 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) CO7D A01N IPC 7 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Category ° Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. --Χ WO 97 13762 A (AGREVO) 1-7,9-2317 April 1997 (1997-04-17) cited in the application claims 2,3; examples 122,195 FR 2 124 427 A (WARNER LAMBERT) 1 - 3Α 22 September 1972 (1972-09-22) claim 3D; example 4 CHEMICAL ABSTRACTS, vol. 108, no. 27, Α 1,2,9-23Columbus, Ohio, US; abstract no. 186576u, page 689; XP002194558 abstract & JP 62 228001 A (TAKEDA) 6 October 1987 (1987-10-06) Further documents are listed in the continuation of box C. lχ Patent family members are listed in annex. ° Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance earlier document but published on or after the international "X" document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L"-docurrent which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 7 November 2002 15/11/2002 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, .. __Francois, J Fax: (+31-70) 340-3016

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